

# A Manganese Dimer Covalently Linked to Ruthenium *tris*-Bipyridine Complex. Towards Mimicking the Electron Donor Side of Photosystem II

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By mimicking the electron donor side of Photosystem II (PS II), we have synthesised and characterized supramolecular model systems in which manganese complexes and tyrosine are electron donors. The donors have been covalently linked to a photosensitizer, ruthenium(II) *tris*-bipyridyl complex, that plays the role of chlorophylls P<sub>680</sub> in PS II. It has been demonstrated that, in the presence of an external electron acceptor in solution, such systems can undergo an intermolecular electron transfer from the photoexcited state of Ru(II) to the acceptor, followed by a subsequent intramolecular electron transfer from the co-ordinated Mn complexes or tyrosine unit to the photogenerated Ru(III), leading to oxidation of Mn complexes or generation of tyrosine radical and regenerating Ru(II). This process is closely mimicking the photoevents on the donor side of PS II. So far, three-step photoinduced electron transfers have been demonstrated.

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# Enhanced Photocurrents from a Self-Assembled Monolayer of a Ruthenium Complex-Viologen 1:2 Linked Thiol Derivative

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Fabrication of very-thin molecular assemblies in which a photoredox pair is elaborately arranged on the electrode surface at molecular levels is one of the promising methods for designing highly-efficient photoelectric conversion systems. How to reduce the reverse electron-transfer in the photoredox pair is an important key for improving the photocurrent efficiency. The present study describes photochemical and photoelectrochemical properties of a ruthenium tris (2,2'-bipyridine) (Ru)-viologen (V) 1:2 linked disulfide intended for reducing the reverse electron-transfer in the self-assembled monolayer (SAM) on the electrode

The 1:2 linked compound (RuC V<sub>2</sub>C S) was prepared in our laboratory in a similar manner as the corresponding 1:1 linked compound (RuC VC S) and the ruthenium compound without the viologen moiety (RuC S). Cyclic voltammetric measurements suggested no electronic interactions between the Ru and the V moieties in the both linked compounds. Luminescence intensities of the three compounds in solution were in the order of RuC S > RuC VC S >> RuC V<sub>2</sub>C S, indicating efficient electron-transfer quenching in the 1:2 compound in the photoexcited state of the Ru moiety.

Photocurrent measurements were carried out with a three electrode cell: the modified electrode, a platinum counter electrode, and a Ag/AgCl (3M NaCl) reference electrode. The light from a Xenon lamp (300 W) was passed through a monochromator and irradiated the modified electrode. The photocurrent action spectrum of the RuC V<sub>2</sub>C S /Au electrode in the presence of 0.01 M triethanolamine (TEOA) had a broad band at ~400 nm ~ 500 nm, characteristic of the electronic absorption band of the Ru moiety as in the case of the RuC VC S/Au electrode [1, 2]. Thus the Ru moiety acts as a photoactive site. The efficiency of photocurrents was higher for the RuC V<sub>2</sub>C S /Au electrode, if the comparison was made in terms of the identical concentration of the Ru moiety. The results suggest that the two viologen moieties cooperate for the enhanced photocurrent efficiency in the SAM. Detailed studies on the photocurrent mechanism are underway.

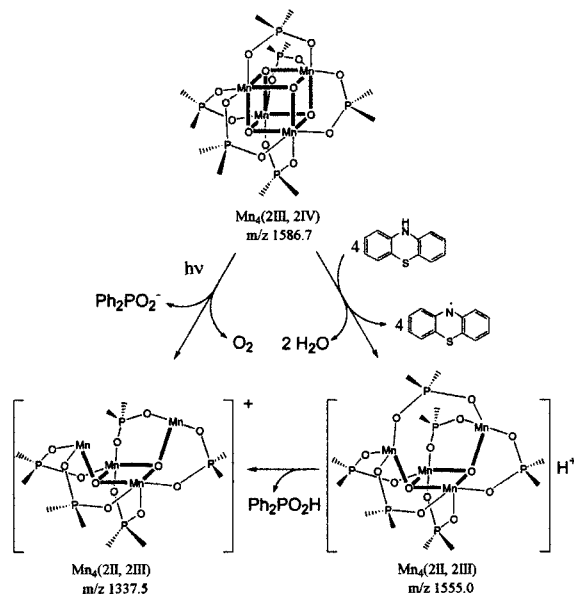
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# Water splitting without photosynthesis: Oxygen evolution by an inorganic mimic of the photosynthetic enzyme

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Photosynthesis produces molecular oxygen ( $\text{O}_2$ ) from water. This process is catalyzed by an enzyme (WOC) whose active site contains an inorganic core comprised of  $\text{Mn}_4\text{O}_x\text{Ca}_1\text{Cl}$  and is known to be organized as a tetramanganese-oxo cluster of incompletely established structure. An early proposed mechanism hypothesized that a  $[\text{Mn}_4\text{O}_4]^{n+}$  cubane core may promote intramolecular O-O bond formation and release  $\text{O}_2$  by conversion to a deoxygenated  $[\text{Mn}_4\text{O}_2]^{n+}$  butterfly core. We have synthesized an artificial water splitting system, inspired by the photosynthetic core, which directly addresses this question for the first time. It consists of a new class of tetra-manganese-oxo clusters,  $\text{Mn}_4\text{O}_4(\text{O}_2\text{PPh}_2)_6$  (**1**), containing the first example of an all oxo-manganese cubane core,  $\text{Mn}_4\text{O}_4^{6+}$ , coordinated to six facially bridging diphenylphosphinate anions ( $\text{Ph}_2\text{PO}_2^-$ ). Complex **1** and its derivatives can be formed in high yield using organophosphinates, which have been proposed as geochemical precursors to phosphates on the early earth. Thus, derivatives of **1** may have existed as chemical precursors prior to photosynthesis. **1** undergoes stoichiometric reduction with various H atom donors (phenothiazine in Fig.) to produce  $\text{Mn}_4\text{O}_2(\text{O}_2\text{PPh}_2)_6$  and releases two water molecules from the corner oxos. This process mimics the reverse process of water binding and oxidation by the WOC by conversion between the  $\text{Mn}_4\text{O}_4^{n+}$  cubane and  $\text{Mn}_4\text{O}_2^{n+}$  butterfly cores. Thermodynamic estimates show that the release of  $\text{O}_2$  from **1** to form  $\text{O}_2 + \text{Mn}_4\text{O}_2(\text{O}_2\text{PPh}_2)_6$  is predicted to be highly exergonic, but is not observed at  $25^\circ\text{C}$  due to a kinetic barrier. This barrier can be overcome both photolytically and thermally. UV laser excitation of a charge-transfer electronic band causes efficient gas-phase fragmentation of photoexcited **1** *via* ejection of  $\text{O}_2$  and one phosphinate:  $\text{Mn}_4\text{O}_4(\text{O}_2\text{PPh}_2)_6^* \rightarrow \text{Mn}_4\text{O}_2(\text{O}_2\text{PPh}_2)_5^+ + \text{O}_2\text{PPh}_2^- + \text{O}_2$ . Both quadrupole/electron-impact and laser-desorption/time-of-flight mass spectrometers confirmed these photo-products. Experiments with the  $\text{L}_6\text{Mn}_4(^{18}\text{O})_4$  isotopomer yielded exclusive formation of  $^{18}\text{O}_2$ , indicating intramolecular oxidation of the  $\mu_3$ -oxo bridges. No evidence for photolytic  $\text{O}_2$  release from **1** was observed without concomitant release of one phosphinate, nor phosphinate release without  $\text{O}_2$  release. Thus, the kinetic barrier to release of  $\text{O}_2$  from cubane **1** appears to be removal of a single phosphinate to form a stable butterfly (jack-in-the box mechanism). In the solid state, programmed heating of **1** releases  $\text{O}_2$  at  $230^\circ\text{C}$  in a stoichiometric reaction, indicating that the kinetic barrier can also be overcome by mild heating. The above reactions appear to be unique to the  $\text{Mn}_4\text{O}_4$  cubane core type and are not found with simpler dimeric  $\text{Mn}_2\text{O}_2$  core complexes. The conversion of **1** to water by reduction and to  $\text{O}_2$  by illumination raises the interesting possibility that solar photochemistry may have directly produced  $\text{O}_2$  from water, non-photosynthetically, using inorganic  $\text{L}_6\text{Mn}_4\text{O}_4$  cubanes in the early archaean geosphere. This process might have been adopted by nature upon evolution of the first  $\text{O}_2$ -producing bacteria. Supported by the NIH (GM39932) and JSPS.



# THE RESEARCH ON SOLAR ENERGY-CHLOROPHYLL CELL

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## ABSTRACT

In the process of the transformation of the solar energy photoelectricity, the solar energy silicon cell is usually used. But owing to the confinement of light wavelength, the light energy of certain wavelength scope in the solar spectrum can be used. Thus, the transformation efficiency of solar energy is lower and 10% or so can only be achieved.

In order effectively to make use of solar energy, the transformation of total wavelength region must be gone on. Making use of the activation effect of chlorophyll under solar energy illumination, solar energy -chlorophyll cell can be developed, which can make the photoelectricity transformation efficiency of solar energy reach 60% or so.

Firstly, this paper introduces the structure piled up to the layer form of chlorophyll. Owing to the fact that the chlorophyll is a kind of photosensitive material, under the effect of sunlight, the activation effect which is produced and the electronics is also produced. Secondly, this paper analyses the course of transplanted electronics is produced under the light guidance. When the electronics transition from high energy level to low energy level, the energy will be released. Making use of the oxidoreductase crowd of chlorophyll, the energy released by the electronics transition is stored, thus the full course of the transformation of photoelectricity has been completed. Finally, this paper introduces the photoelectricity transformation course of chlorophyll.

# Carotenoids in Artificial Photosynthetic Media: Photodegradation, Excited State Lifetimes, and Energy Transfer

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DMPC (dimyristoyl-L- $\alpha$ -phosphatidylcholine) liposomes are used as artificial photosynthetic media to study the behavior of carotenoids. 8'-Apo- $\beta$ -caroten-8'-al (**I**) and  $\beta$ -carotene (**II**) degrade faster under irradiation in DMPC liposomes than in organic solvents, which may be because vibrational deactivation of carotenoid excited states is less efficient in rigid lipid membranes. The lifetime of the first excited singlet state ( $S_1$ ) of **I** in DMPC liposomes is 27.2 ps, very close to that in 3-methylpentane (26.4 ps), but longer than its lifetime in EtOH (17.1 ps) or CH<sub>2</sub>Cl<sub>2</sub> (14.1 ps). The lifetime of the  $S_1$  state of **I** in DMPC liposomes is as expected for an alkane environment. The lifetime of the  $S_1$  state of **II** in DMPC liposomes is 10.3 ps, similar to its lifetime in 3-methylpentane (8.1 ps), EtOH (9.2 ps) and CH<sub>2</sub>Cl<sub>2</sub> (8.5 ps). This independence of the  $S_1$  state lifetime of **II** on the matrix agrees with earlier observations. Carotenoid **I** can suppress the photodegradation of chlorophyll a (Chl a) in liposomes, which shows the protection role of **I** on Chl a under strong irradiation. In liposomes, Chl a fluorescence quenching by **I** is observed when using either the  $Q_y$  band or the Soret band of Chl a as the excitation line. This observation suggests that the  $S_1$  state of **I** is lower than the  $Q_y$  state of Chl a, and that energy can transfer directly from the  $Q_y$  state of Chl a to the  $S_1$  state of **I**. This work is supported by the Division of Chemical Science, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

# Molecular Catalysts for Dark Water Oxidation as Photosynthetic Oxygen

## Evolving Center Models

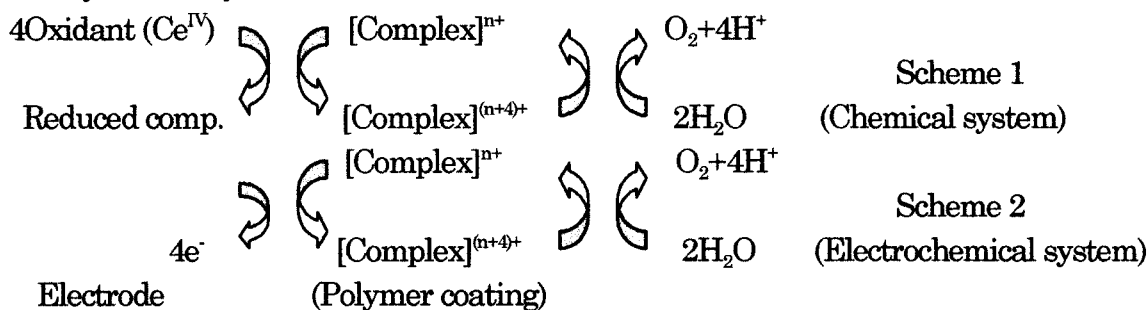
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Water oxidation catalysis is an important reaction for artificial photosynthetic systems that aim at creating new energy resources from solar energy and water<sup>1-3</sup>. This is the step to utilize water as an electron donor. There have been only few artificial examples of active molecular catalysts for water oxidation because of the difficulty of the 4-electron process involving two water molecules ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$ ).

We have investigated dark water oxidation catalysis by metal complexes by chemical and electrochemical methods (Schemes 1 and 2), and found that ammine Ru complexes have high catalytic activity for water oxidation<sup>2,3</sup>.



Important points found are as follows<sup>3</sup>:

- 1) The number of molecule needed for the 4-electron reaction depends on the structure.  
4-e catalysts:  $[(\text{NH}_3)_5(\mu\text{-O})\text{Ru}(\text{NH}_3)_4(\mu\text{-O})\text{Ru}(\text{NH}_3)_5]^{6+}$  (Ru-red),  $[(\text{NH}_3)_5\text{Ru}(\mu\text{-O})\text{Ru}(\text{NH}_3)_5]^{4+}$ ,  $\text{cis-}[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^+$ , 2-e catalysts:  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ ,  $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^+$
- 2) For the 2-electron catalysts, cooperative catalysis by two catalyst molecules takes place.
- 3) The catalysts undergo bimolecular decomposition causing oxidation of the ammine ligand to N<sub>2</sub>, but are stable when they are isolated with each other
- 4) Isolation of the catalysts by incorporating in a matrix such as a polymer membranes is remarkably effective for stabilization against bimolecular decomposition.
- 5) For electrochemical catalysis using polymer[catalyst]-coated electrode, charge transport to the catalysts by charge hopping is important. Amino acid residue models enhances the catalysis to a great extent by lengthening the charge hopping distance to twice.

Coupling of the catalysts with a photoexcitation center is now under way.

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# Solar Energy Conversion at Liquid-Liquid Interfaces.

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The amount of solar energy incident on the Earth is about  $5 \cdot 10^{21}$  kJ per year, of which  $3 \cdot 10^{18}$  kJ is converted into chemical energy by photosynthesis in plants and microorganisms. This light energy is harvested by photosynthetic pigment systems in which the electronic structure of excited-state chlorophyll donates an electron to a primary acceptor pheophytin, the first component of an electron transport chain. The electron carries with it the energy of the original photon of light that was absorbed, and in the process of electron transport the energy is captured in two ways [1]. The first involves coupling a proton pump mechanism coupled to the sequential redox reactions in one part of the electron transport chain, so that a proton gradient is established across the thylakoid membrane. The electrochemical energy of the proton gradient is then used to drive ATP synthesis by the ATP synthase enzymes embedded in the membrane. The second energy capture occurs when an acceptor molecule such as NADP is reduced to NADPH, which in turn is used to reduce carbon dioxide in the Calvin cycle. Systems modeling photosynthesis should have the capability of carrying out relatively simple versions of these fundamental reactions.

The interface between two immiscible liquids with immobilized photosynthetic pigments can serve as a convenient model for investigating photoprocesses that are accompanied by spatial separation of charges [1-4]. The efficiency of charge separation defines the quantum yield of any photochemical reaction. Heterogeneous systems will be most effective in this regard, where the oxidants and the reductants are either in different phases or sterically separated. Different solubilities of the substrates and reaction products in the two phases of heterogeneous systems can alter the redox potential of reactants, making it possible to carry out reactions that cannot be performed in a homogeneous phase.

Four types of artificial photosynthetic reactions at the oil/water interface were studied in our research group: (1) Photoredox reactions at the interface between two immiscible liquids; (2) Phototransfer of ions or electrons across or along oil/water interfaces; (3) Photochemical reactions in one phase following extraction of products in two different phases; (4) Coupled photochemical and redox reactions.

The present work focuses on electrochemical mechanisms of photocatalytic systems at the oil/water interface. In order to provide a biological perspective, we will first describe the charge transfer processes that occur at liquid/liquid interfaces in green plants.

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# **Electron Transfer Studies of Different Ruthenium-Manganese Compounds on TiO<sub>2</sub>**

## **– A System that Mimics Nature?**

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The oxidation of water that occurs in green plants has fascinated mankind for many decades. Still today is the idea of creating an artificial system that mimics nature by oxidizing water a hot subject.

When a green plant absorbs light from the sun a series of electron transfer reactions are initiated. First the photoactive chlorophylls in Photosystem II are excited by the sunlight and thereafter oxidized through an electron transfer to a primary acceptor. The electron is then stepwise transferred until it reaches a final acceptor. To make the plant ready for another photon from the sun the photoactive part has to be reduced. Nature has solved this by using water as electron source. To abstract electrons from water the photoactive part is reduced again through an electron transfer from a manganese cluster. When this manganese cluster has transferred four electrons it is re-reduced through the oxidation of two water molecules.

To mimic this process we have synthesized several systems consisting of a ruthenium-based part as photo-sensitizer connected to different manganese ligands. Earlier studies in solution have shown that intramolecular electron transfer from the manganese to the photo-oxidized ruthenium(III) do occur. To stabilize higher oxidation states of the manganese, a new manganese dimer with negative ligands has been synthesized and linked to a ruthenium complex. In this study we will investigate this compound attached onto nanocrystalline TiO<sub>2</sub>, using photo electrochemistry and time-resolved spectroscopy to see how both photocurrent properties and electron transfer reactions are affected in the absence and presence of manganese.



## **Steady-state, contact-less photo-conductivity action spectra of bilayers of TiO<sub>2</sub> and organic molecular antenna systems.**

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Recently it has been shown that bilayer junctions of a p-type conducting polymer and a smooth thin layer of TiO<sub>2</sub> are potential candidates to function in solid state solar cells <sup>[1,2]</sup>. In such a device the polymer functions both as the antenna / electron injection layer as well as the conducting layer for the hole transport. One of the factors that is limiting the efficiency of such a construction is the exciton diffusion length in the polymer layer which determines to what extent the excitation energy will migrate to the photoactive interface. In this work the exciton diffusion length of several polymers is investigated in more detail by recording steady-state (intensity modulated) action spectra of the photo-conductivity of several polymer-TiO<sub>2</sub> bilayer junctions. By modeling the efficiency and wavelength dependence upon illumination directly into the photoactive interface (from the side of the TiO<sub>2</sub>) and upon illumination from the side of the polymer a careful determination of the exciton diffusion length and the wavelength dependence of the electron injection efficiency of several polymer and other antenna molecules will be determined. The conductivity is detected via the so-called microwave conductivity technique, which has the advantage that it is not necessary to connect metal electrodes to the sample.

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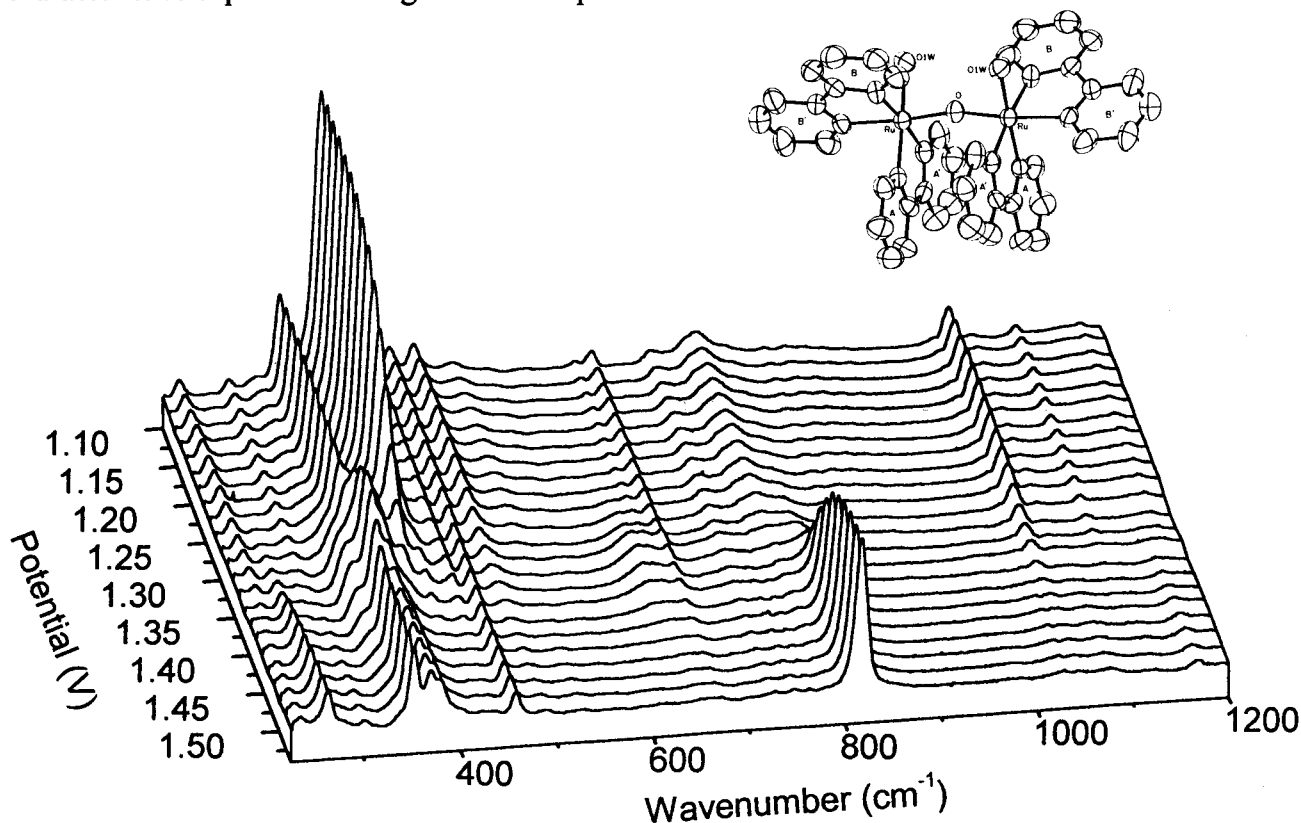
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# Structural Characterization and Dynamics of Higher Oxidation States of the Water Oxidation Catalyst, $\text{cis,cis-}[(\text{bpy})_2\text{Ru}(\text{OH}_2)]_2\text{O}^{4+}$

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Use of a columnar-flow carbon fiber electrode has enabled us to prepare for the first time clean solutions of highly oxidized ruthenium  $\mu$ -oxo dimers in strongly acidic media. Three oxidation states above the  $\text{Ru}^{\text{III}}\text{-O-Ru}^{\text{III}}$  ion were detected by resonance Raman (RR) and optical spectroscopies. These were assigned to the  $\text{Ru}^{\text{III}}\text{-O-Ru}^{\text{IV}}$ ,  $\text{Ru}^{\text{IV}}\text{-O-Ru}^{\text{IV}}$ , and  $\text{Ru}^{\text{V}}\text{-O-Ru}^{\text{V}}$  oxidation states by redox titration with  $\text{Os}(\text{bpy})_3^{2+}$  and analysis of the reaction product formed between the  $\text{Ru}^{\text{III}}\text{-O-Ru}^{\text{III}}$  and most highly oxidized species. The  $\text{Ru}^{\text{V}}\text{-O-Ru}^{\text{V}}$  ion underwent first-order decay to form the  $\text{Ru}^{\text{IV}}\text{-O-Ru}^{\text{IV}}$  ion, which subsequently decayed more slowly by a complex mechanism. The rate constant for  $\text{Ru}^{\text{V}}\text{-O-Ru}^{\text{V}}$  disappearance coincided with the catalytic rate constant for  $\text{O}_2$  formation under steady-state conditions, indicating that the  $\text{Ru}^{\text{V}}\text{-O-Ru}^{\text{V}}$  ion is either the  $\text{O}_2$ -evolving species or an immediate precursor to it. Low-temperature RR spectra indicated that  $\text{Ce}^{4+}$  associated with the higher oxidized forms by coordinating to the cis ruthenyl oxo atoms, presumably forming cyclic trinuclear structures. Low-temperature epr spectra of electrochemically prepared  $\mu$ -oxo dimers also gave evidence for aggregation in the absence of  $\text{Ce}^{4+}$ , suggesting formation of cofacial dimer-of-dimer structures. An unusual narrow  $g = 2$  signal was observed in the low-temperature spectrum of the  $\text{Ru}^{\text{V}}\text{-O-Ru}^{\text{V}}$  ion which had the characteristics expected for a ligand radical species.



RR spectroelectrochemical titration of the  $\mu$ -oxo dimer showing progress formation of the  $\text{Ru}^{\text{III}}\text{-O-Ru}^{\text{IV}}$ ,  $\text{Ru}^{\text{IV}}\text{-O-Ru}^{\text{IV}}$ , and  $\text{Ru}^{\text{V}}\text{-O-Ru}^{\text{V}}$  ions; (molecular structure from Gilbert et al. (Meyer), *JACS*, 107, 3855-3864 (1985)).

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**NMR-spectroscopy as a direct method to identify the localization of the paramagnetic forms of reversible electron carriers in the lipid bilayer: study of the localization of cetylviologen cation-radical in the suspensions of lipid vesicles**

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Identification of spatial localization of the individual components of electron-transport chains in natural and artificial bilayer membranes is of principal importance for study of mechanisms of many primary redox biological processes as well as for elaboration of biomimetic systems, for example, those modeling natural photosynthesis. The known direct methods of determination of such localization of namely functional molecules are usually very laborious. Therefore, for providing such studies in practice instead of these molecules their analogs or special molecules-labels (for example, paramagnetic spin-labels, etc.) are often used.

We have found that for paramagnetic forms of reversible electron carriers, the NMR-spectroscopy allows receiving a **direct** information on their localization, because the paramagnetic lipophilic electron carriers influence selectively the  $^1\text{H}$  NMR spectra of the molecules constitutive the bilayer lipid membranes.

The capacity of the NMR method has been tested on an example of the widely used lipophilic electron carrier cetylviologen (N,N'-dihexadecyl-4,4'-dipyridinium dibromide). It was established [1] that the paramagnetic cation-radical of cetylviologen influences mostly the signal of the  $^1\text{H}$  NMR spectra of the  $-\text{N}^+(\text{CH}_3)_3$ , which are localized on the surface of the vesicle membrane, while all other NMR signals of the lipid remain unchanged. A remarkable change in the width of this signal corresponds to localization of the radical paramagnetic center (i.e. of the aromatic groups of the electron carriers) on the surface of the vesicle membrane and to a fast lateral diffusion of the lipid molecules around the radical.

Reference:

**Photochemical activity of CdS nanoparticles, made from lipophilic cadmium complexes, in the process of electron phototransfer through the lipid vesicle membranes**

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The importance of solar energy conversion and storage has prompted the vigorous investigation of photoinduced transmembrane electron transfer in artificial model systems such as unilamellar vesicles. The existent models are yet not as efficient as natural photosynthesis due to the failure in design of an efficient electron transfer chain across the bilayer lipid membrane [1]. The spatial organization of the semiconductor nanoparticles driven electron-transport chains in these models might be improved upon using the lipophilic cadmium complexes (dithiocarbamates, xantogenates and so on) which can serve as precursors of cluster cadmium sulfide nanostructures. These complexes can be built in the lipid bilayer membrane due to their lipophilic properties, that allows to deep generated from the nanoparticles of a cadmium sulfide in lipid bilayer membrane.

Moreover, the usage of the presynthesized cluster cadmium sulfide compounds allows to avoid the step of injection of the free sulfides anions into the system which is necessary at common methods of synthesis of the CdS nanoparticles. This is of a serious importance for studying the mechanism of the photoinduced electron transference, since in this case there is no excess of sulfide anions, which can provide a “dark” reduction of the electron carriers.

The nature of the CdS precursors influences substantially the size of the generated sulfide particles and their size distribution, as well as some sufficient parameters of lipid vesicles, in particular, their stability and sizes.

The preferential places of cluster cadmium sulfide nanostructures localization seem to be the outside surfaces of the lipid membrane vesicles.

We examined the photochemical activity of the synthesized CdS clusters. In particular, it was detected, that usage of the hydrophylic electron donors as well as of hydrophylic electron carriers enlarges the quantum yield of photogeneration of the reduced forms of electron carriers, for example, methylviologen, as contrasted to cethylviologen.

Reference:

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# Energy and Electron Transfer in Bichromophoric Molecules: The Effect of Symmetry and Donor/Acceptor Energy Gap

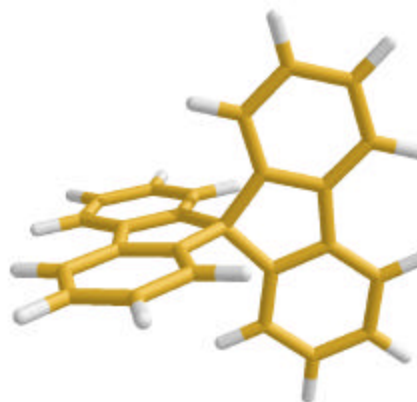
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The dependence of the rate of singlet excitation transfer on the donor-acceptor energy gap was investigated in bichromophoric spiranes with symmetry forbidden zero-order electronic coupling. The fluorescence measurements were performed in a supersonic jet in order to avoid collisional and inhomogeneous line broadening. Although the transition moments of the linked chromophores are rigorously perpendicular, and the exchange coupling between the  $\nu' = 0$  states is computationally shown to be zero, all spiranes with energy gaps larger than  $\sim 1000\text{ cm}^{-1}$  exhibited complete electronic energy transfer from all vibrational states of the electronically excited donor, including the undistorted  $\nu = 0$  state. This behavior is explained in terms of vibronic coupling between the sparse states of the donor and the dense manifold (pseudo-continuum) of the acceptor states. The electronic energy transfer was sufficiently fast to result in measurable lifetime broadening of the donor lines, from which the  $k_{\text{ET}}$  was estimated. Only at the bottom of the vibrational manifold of nearly degenerate spiranes (energy gaps smaller than  $200\text{ cm}^{-1}$ ) strict MO symmetry control of excitation transfer was observed.

## SPIROBIFLUORENE



MO symmetry forbidden photoinduced electron transfer was studied in solution in suitably substituted donor-acceptor spirobifluorenes. Similarly as in the gas phase, rapid transfer rates and strong vibronic coupling (effective  $V_{\text{DA}} \approx 200\text{ cm}^{-1}$ ) were observed. The results demonstrate that the zero-order picture severely overestimates the degree of the molecular orbital symmetry control over electronic energy transfer and charge transfer rates, and that at sufficiently high driving forces the vibronically mediated "symmetry forbidden" electronic energy transfer can be very rapid ( $\sim 1 \times 10^{12}\text{ s}^{-1}$ ).

The results of the most recent extension of this work, which involves novel donor-acceptor systems linked by a heteroatom in the spiro- position (  $>\text{Si}<$ ,  $>\text{Ge}<$  and  $>\text{Sn}<$  ), will be also discussed.

# A Metalloradical Mechanism for Structure Phototransformations in Chromated Denatured Polypeptides

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The significant components of photosynthetic reaction centers in plants and photoactive bacteria are complexes of photoactive molecule, polypeptide chain, acceptor and metallocaster. The important role in such complexes play one- and multy-electron processes. As a model of some elements in such systems one can consider lightsensitive layers of proteins with transition metal compounds. Among their number the collagen complexes with a strong electron acceptor - chromium oxyanions are worthy of attention.

The photoreduction of chromium (VI) oxyanions and photooxidation of polypeptide chains as it have been shown in our studies are accompanied by the changing of the molecular and supramolecular structure of the denatured protein. One can consider them as cristallization - amorphization processes. They can have a latent or obvious character. This process is essentially influenced by water and oxygen. The photostructural transformations were find out to have reversible dispositions for some conditions.

The result of the light action is formation of primary one-electron reactions products - chromium (V) compounds and free radicals or ion-radicals. One can registrate the products of multyelectron processes in the presence of water or oxygen. Studying the reversible transformations of the chromium (V) formation and desease the effect of the reversible change of their magnetic features was found out. The g-factor of Cr (V) has been shown to be changed discretively ( $g_{\text{light}}=1.970$ ,  $g_{\text{dark}}=1.961$ ). The amplitude of ESR signal remains practically constant at the same expositions.

Usually chromium (V) compounds are thought to be active oxidative agents much more stronger than chromium (IV) or chromium (III) compounds. But rather unexpectedly we displayed that some chromium (V) compounds could be active reducing agents ( $E_{1/2}=-0.50$  v). This gives a ground to consider that reversible processes in the investigated systems can have not only structural but also redox character and sooner combined one. The study in model alcohol systems showed formation under light action in charge transfer band ( $\lambda$  441 nm) of the light sensitive product (absorption maximum at  $\lambda$  630 nm). It can be connected with relaxation of the forbidden singlet-triplet transaction in chromium oxyanions or can be explained by metalloradical pair formation.

A result of light-exposition of denatured protein samples was decreasing of their electroconductivity and refractobility changing. After the water treatment they increased again. Generations of charged products and migration of cation-radial states (holes) leng-wise protein chains and the changes of structure connected with them are discussed.

The results are minded to be deal with the problem of solar energy conversion and possible enviroment chemistry for detoxification of transition metal compounds and organics.

## **Steric Effects and Electron Transfer Influence on Excited States Deactivation in Sterically Hindered Porphyrins and Their Chemical Dimers**

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Conformational distortions of non-planar tetrapyrrole chromophores play an important role in controlling photophysical and photochemical events in photosynthetic antenna and reaction centre protein complexes. In addition, synthetic porphyrins and their dimers, covalently linked to various electron acceptors are widely used to model some aspects of photosynthetic electron transfer (ET) events. In some cases, in order to understand ET pathways through bond or through space the porphyrin-acceptor molecule contains an inserted phenyl ring between the redox pair.

Using steady-state and nanosecond pump-probe spectroscopy we observed for the first time that mono- and di-*meso*-phenyl substitution in sterically hindered octaethylporphyrins, OEP (free bases, Zn- and Pd-complexes) as well as the formation of OEP chemical dimer with the phenyl ring as a spacer lead to the strong shortening of triplet lifetimes (from ms to ns) and phosphorescence quantum yields decrease (by ~250-2500 times) at 293 K in degassed toluene solutions without any influence on spectral-kinetic parameters of  $S_0$  and  $S_1$  states. This quenching accompanied by the appearance of new bands ( $\lambda \sim 1000$  nm) in T-T transient spectra is caused by torsional librations of the phenyl ring around a single C-C bond leading to non-planar dynamic distorted conformations realised in the excited  $T_1$  states namely.

For OEP's with electron-accepting  $\text{NO}_2$ -groups the strong non-radiative deactivation of  $S_1$  and  $T_1$  states (by ~2-3 orders of magnitude) is found upon the displacement of  $\text{NO}_2$ -group from *para*- and *meta*- to *ortho*-position of the phenyl ring. For OEP-Ph(*meta*- $\text{NO}_2$ ), OEP-Ph(*para*- $\text{NO}_2$ ) molecules and OEP chemical dimers with the same substitution, photoinduced ET processes with the participation of  $S_1$  state are affected by through-bond interactions. In contrast, for OEP-Ph(*ortho*- $\text{NO}_2$ ) molecule the direct through-space ET from the porphyrin  $S_1$  state to the low-lying CT state of the radical ion pair is very effective ( $k_{\text{et}}^S = 9.5 \times 10^9 \text{ s}^{-1}$ ). The  $T_1$ -state additional deactivation in OEP's is caused by thermally activated transitions to upper-lying CT states of the radical ion pair and the strengthening of rate constants of non-radiative  $S_1 \rightarrow T_1$  transition.

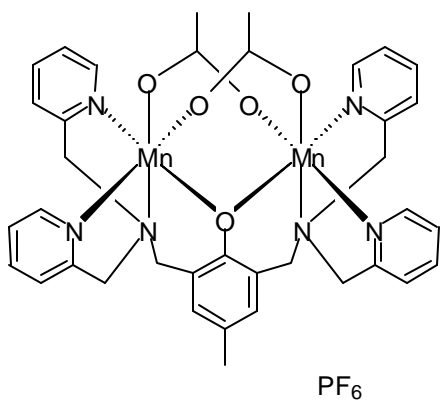
On the other hand, upon *meso-ortho*-nitrophenyl substitution the strong phosphorescence quenching of Pd-octaethylporphyrins at 293 K (by  $>10^4$  times) is due to the direct non-adiabatic through-space ET from  $T_1$  state to the low-lying CT state of the radical ion pair ( $k_{\text{et}}^T = (1.5-4.0) \times 10^9 \text{ s}^{-1}$ ). Transient absorption spectra of all *ortho*-nitrophenyl substituted OEP's in the region of 1100-1400 nm are formed by the mixing of pure  $\pi\pi^*$ -states and charge-transfer states.

## Possible Ligand Exchange in the Manganese Cluster of Synthesized “PSII” Model Systems.

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In our work which is part of the E.C. subsidized TMR program “Ru-Mn Artificial Photosynthesis” we try to synthesize complexes that mimic the function of PSII. The



main motivation for this research is that we want to oxidize water, driven by light energy, and use the liberated electrons to produce reduced fuels, *e.g.* hydrogen. On this poster we will focus on the manganese part (the putative water splitting complex) of our model complexes.

Using cw-EPR we studied the light-induced oxidation of a synthesized Manganese<sup>II-II</sup> dimer

both in an inter- and intra-molecular system using a Ruthenium complex as the photosensitizer (the primary donor of our model systems). In both cases we observe the stepwise oxidation of the Manganese<sup>II-II</sup> dimer up to a Mn<sup>III-IV</sup> mixed valence state. Work on this is presented in the poster of Ping Huang-Kenez.

On this poster we will present experiments that indicate ligand exchange at our Manganese cluster. That is, the possible reversible exchange of the mu-aceto bridges for co-ordinated water resulting in the loss of the weak anti-ferromagnetic coupling between the two Manganeses within the Mn<sup>II-II</sup> dimer. This ligand exchange is thought to stabilize the higher oxidation states of the Manganese dimer and is a prerequisite for the putative water splitting capacity of the complex.



# **Luminescence of Europium Complexes with Trifluoroacetic Acid**

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Europium complexes with trifluoroacetic acid of composition  $\text{Eu}(\text{TFA})_3 \cdot 2\text{D} \cdot n\text{H}_2\text{O}$  and  $\text{Eu}_{1-x}\text{Gd}_x(\text{TFA})_3 \cdot 3\text{H}_2\text{O}$ , where TFA is an anion of trifluoroacetic acid, D is 1,10-phenanthroline (Phen), 2,2'-bipyridyl (bipy), triphenylphosphine oxide (TPPO), dimethylsulfoxide (DMSO), dimethylformamide (DMFA), benzotriazol (BTA), hexamethylphosphorous triamide (HMPT) ;  $x=0-0,7$  were synthesized. The compounds are characterized by elemental analyses and IR and luminescence spectra. It is show that the functional groups of anions in complexes are coordinated as monodentate or bridging ligands.

Photo-, thermostability and intensity of luminescence of these compounds were investigated. The complexes  $\text{Eu}(\text{TFA})_3 \cdot 2\text{D} \cdot n\text{H}_2\text{O}$  proven to be resistant to ultraviolet irradiation. The luminescence intensity is enhanced with time for 2,5 h. Part of the bridging groups in the compound seems to break upon exposure to the ultraviolet irradiation. A drastic decrease in luminescence intensity, which is observed upon further irradiation exposure, is indicative of degradation of the complex.

The sensitization influence of Gd(III) on the intensity of europium ion luminescence was stated in  $\text{Eu}_{1-x}\text{Gd}_x(\text{TFA})_3 \cdot 3\text{H}_2\text{O}$ . Luminescence spectroscopic evidence and the examination of excitation spectra indicate the occurrence of efficient energy transfer from the gadolinium to the europium ion. The greatest promotion of  $\text{Eu}^{3+}$  fluorescence at 615 nm is observed when  $\text{Eu}:\text{Gd} = 1:1$ .

# Thermoluminescence from the Visible and UV-Irradiated Terbium(III) Complexes

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Thermoluminescence from low temperature UV-irradiated of aromatics and RE-doped phosphors has been investigated by many authors. It has been recognized that the thermoluminescence in many cases is caused by recombination of the charged species generated by the photoionization in the molecule of the complex. The group of the light-transforming coordination compounds REE, possessing ability to the division of the charges under the accumulation of the excitation energy have been isolated for the first time<sup>1</sup>. We at first time discovered that the substances  $[\text{Tb}(\text{NO}_3)_2\text{Acac}(\text{Phen})_2]\text{H}_2\text{O}$ , where Acac- acetylacetone, Phen- 1,10-Phenanthroline, referring to the charge - transfer complexes, may accumulate energy of the photons through separation of the charges with following thermolighting. Substance are isostructuring to the complex  $[\text{Dy}(\text{NO}_3)_2\text{Acac}(\text{Phen})_2]\text{H}_2\text{O}$  crystals<sup>1</sup> of which has builded from the molecules  $\text{Dy}(\text{NO}_3)_2\text{Acac}(\text{Phen})_2$  and  $\text{H}_2\text{O}$ , connecting molecules of the complex by hydrogeniums bonds O-H...O to the endless chains along axis Y. Atom Dy is bonding bidentate with the five ligands (coordination number is 10). Studied complexes are the system which has properties of the charge transfer complexes and including base elements: donor of the electrons (Acac), «switch of the electronic stream» from the one subsystem to the other (Tb, Dy), acceptor of the electrons (two molecules of the Phen). The paramagnetic radicals formed in thermoluminescent complex Tb(III) have been studied using the technique of ESR. Two radicals, assigned to anion-radical and biradical of the Phen, were observed at UV-irradiated at the room and low temperature.

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## **Antenna effects and multiplets in rare-earth ionomers**

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The incorporation of lanthanide ions in suitable host materials has generated great interest in the past few years, because they can impart to these materials some valuable optical properties.

Radical polymerization of Eu(III) and Tb(III) mixed-ligand complexes containing acetylacetone and unsaturated acids (acrylic, methacrylic) with acrylic acid and methylmethacrylate was carried out. Luminescence intensity of monomer complex and Eu(III) MMC with acetylacetonate-ion were shown to be compatible.

Lanthanide-containing macromolecular complexes (MMC) of Eu(III) dibenzoylmethanate with polyacrylic acid containing pendant o-phenanthroline groups were synthesized. The analysis of luminescence excitation spectra of the polymer shows the presence of effective energy transfer from resonance levels of chromophore groups to Eu (III) (antenna effect): luminescence intensity of polymer containing 0,75 wt.% Eu(III) and 2% phenanthroline groups is one order higher than europium polyacrylates.

It was detected that luminescence properties of Eu(III) MMC with styrene-methacrylic acid copolymer depend on polymer composition significantly: the formation probability of multiplets formed from lanthanide ions and functional groups of macromolecular ligand increased with increasing of methacrylic acid content. It was revealed that multiplet formation could promote not to Eu(III) luminescence quenching but to f-f transition intensification due to charge transfer state.

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